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(21) International Application Number: PCT/US98/05407 (22) International Filing Date: 19 March 1998 (19.03.98) (30) Priority Data: 08/850,792 2 May 1997 (02.05.97) US (71) Applicant: ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US). (72) Inventors: NARAYANAN, Kolazi, S.; 33 Carol Place, Wayne, NJ 07470 (US). JON, Domingo; Apartment 28, 41-51 Kenmare Street, New York, NY 10012 (US). IANNIELLO, Robert, M.; 5330 Berkshire Valley Road, Oak Ridge, NJ 07438 (US). (74) Agents: MAUE, Marilyn, J. et al.; International Specialty Products, Legal Dept., Building 10, 1361 Alps Road, Wayne, NJ 07470 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: SOLID DELIVERY SYSTEM (SDS) FOR ACTIVE AGRICULTURAL CHEMICALS (57) Abstract <p>This invention relates to a solid delivery system (SDS) for active agricultural chemicals, and, more particularly, to a bioenhanced, stable SDS for sulfonyl and sulfamoylurea agricultural chemicals capable of forming aqueous microdispersions or tank mixes thereof suitable for application to a plant site.</p>		

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SOLID DELIVERY SYSTEM (SDS) FOR
ACTIVE AGRICULTURAL CHEMICALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a solid delivery system (SDS) for active agricultural chemicals, and, more particularly, to a bioenhanced, stable SDS for sulfonyl and sulfamoylurea agricultural chemicals capable of forming aqueous microdispersions or tank mixes thereof suitable for application to a plant site.

2. Description of the Prior Art

Sulfonyl and sulfamoylurea (SU) herbicides are very susceptible to hydrolysis in water or in admixture with other polar organic solvents which promote proton exchange between such chemicals and the solvent. Particularly, both the sulfonyl and sulfamoylurea compounds have a labile sulfonamide bridge which decomposes readily in water. Accordingly, stabilized liquid emulsifiable concentrates of such herbicides have been developed which when added to water to form a tank mix are suitable for application to a plant site. Such liquid emulsifiable concentrates are described by Narayanan et al. in copending U.S. patent application Serial No. 08/733,285, filed October 17, 1996.

Narayanan, in U.S. Pat. 5,389,297, also has described an inert matrix composition in the form of a free-flowing, high melting solid suitable for making a microemulsifiable concentrate by slurring the active with a small amount of water, and freeze-drying. This concentrate will provide an aqueous microemulsion upon dilution with tank mix water. However, for sulfonyl and sulfamoyl ureas, as described in this invention, it is more advantageous to keep these actives and water apart until the final application step, so as to minimize the hydrolysis effect on such actives, while maximizing the bioenhancing capability of the N-octyl pyrrolidone component of the inert matrix composition on these actives.

SUMMARY OF THE INVENTION

What is described herein is a bioenhanced, stable solid carrier system for one or more sulfonyl or sulfamoyl urea agricultural chemicals suitable for forming an aqueous microdispersed tank mix upon dilution with water, which comprises, by weight, (a) 80-99.5% of an inert matrix composition comprising 10-50% of a C₆-C₁₈ alkyl pyrrolidone, about 5-50% of an anionic surfactant and about 10-70% of a water-soluble, high melting organic compound containing a dissociable proton which can complex with said pyrrolidone, a melting point of > 100°C. a molecular weight of ≤ 500 , and a water solubility of at least 10%, which is selected from the group consisting of hydroxy acids, amino acids, sugars and amides, and (b) 1-20% of said agricultural chemical, optionally with a diluent agricultural chemical.

A further feature of the invention is an aqueous dispersion tank mix comprising dilution water in an amount sufficient to reduce the concentration of the agriculturally active ingredient to between a few ppm and 1% by weight.

Still another aspect of the invention is a method of making such systems which comprises admixture (a) and (b) as separate components.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, the SDS includes (a) an inert matrix composition which comprises a higher lactam, i.e. a C₆-C₁₈ alkylpyrrolidone, e.g. N-octylpyrrolidone, N-isooctylpyrrolidone or N-dodecylpyrrolidone, or mixtures thereof. N-octylpyrrolidone is preferred. The lactam is present in an amount of about 10-50%, preferably 15-40%, and most preferably, 20-30%, by weight.

The second component is an anionic surfactant which is typified by an alkali metal salt of a C₈-C₂₂ aliphatic surfactant such as sodium dodecyl sulfate, or an alkyl aromatic sulfate, or sulfonates, ethoxylated derivatives of the above, alkylphenyl ethoxylated phosphate esters, tristyryl phenyl ethoxylated phosphate esters and the like. Sodium dodecyl sulfate is preferred. The anionic surfactant is present in the amount of about 10-50%, preferably 20-45%, and most preferably, 25-35%, by weight.

The third component is a complexing agent which is characterized by being an organic compound having a

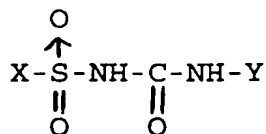
melting point of $> 100^{\circ}\text{C.}$, a molecular weight of ≤ 500 , a water solubility of at least 10%, and being capable of hydrogen-bonding with the higher alkyl pyrrolidone. Suitable complexing agents for use herein have a dissociable proton which are present in hydroxy acids, such as lactic or citric acid; amino acids, such as glycine; sugars, such as lactose, sucrose, glucose or fructose; or amides, such as urea. The complexing agent is present in an amount of about 10-70%, preferably 30-60%, and most preferably, 25-50%, by weight.

Suitably a small amount of water is added to the mixture of components of (a), and the mixture is sprayed, freeze-dried or fluidized to form a solid.

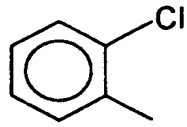
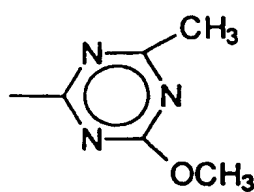
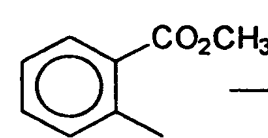
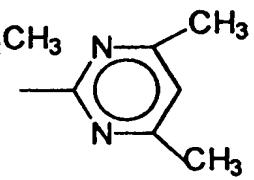
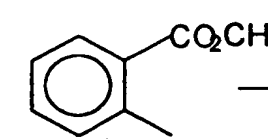
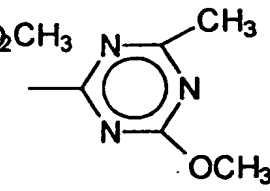
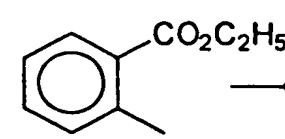
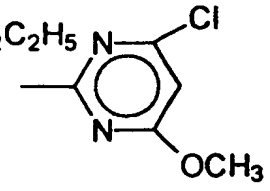
Component (a) then is provided in the form of a free-flowing, high-melting solid, which is usually a granular, hygroscopic, or crystalline solid having a melting point of $>100^{\circ}\text{C.}$

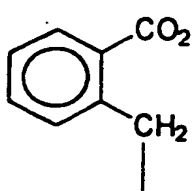
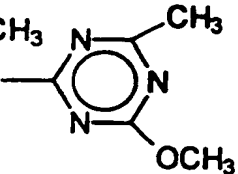
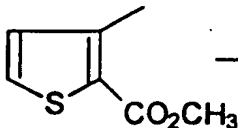
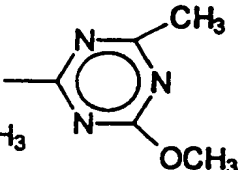
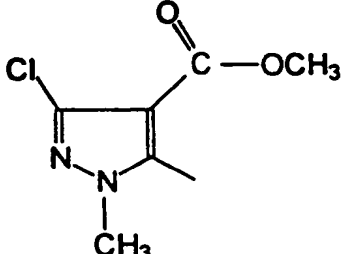
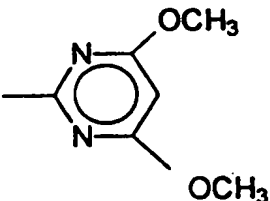
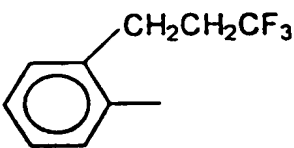
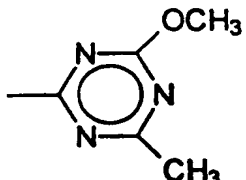
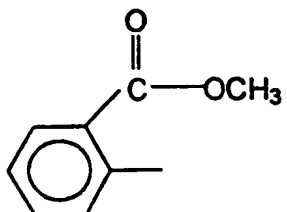
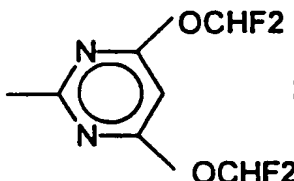
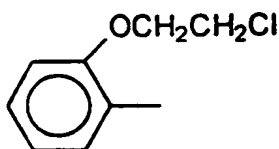
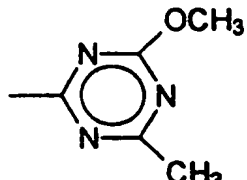
The (a) component then is admixed separately with (b), the SU, to form the desired SDS. Generally the SDS comprises about 80-99.5%, by weight, of (a) and 0.5-20% of (b), preferably 2-15%, and most preferably 3-10% of the SU. Optionally dispersant and/or wetting agents may be included in the SDS to assist in the formation of aqueous dispersions thereof upon dilution thereof with tank mix water. Optionally a hydrophobic polymer, or an inorganic mineral can be added to make the SDS less hygroscopic.

Typical active agricultural chemicals for use herein are shown below.

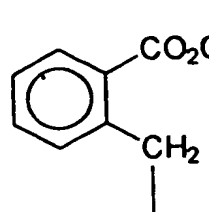
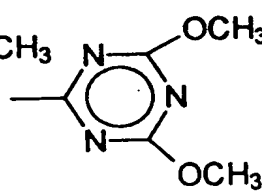
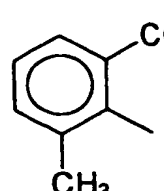
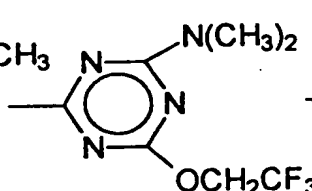
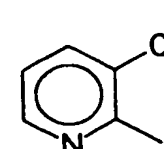
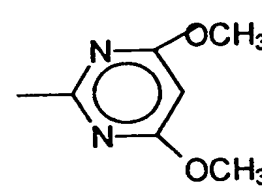
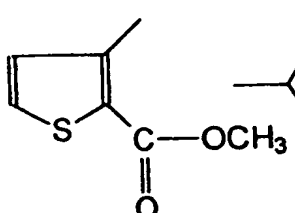
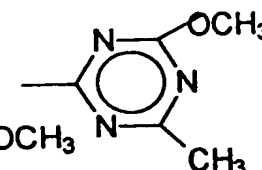


where X and Y are selected from the following:

X	Y	NAME	
		Chlorsulfuron	Du Pont
		Sulfometuron methyl	Du Pont
		Metsulfuron methyl	Du Pont
		Chlorimuron ethyl	Du Pont

X	Y	NAME	
		Bensulfuron methyl	Du Pont
		Thifensulfuron methyl	Du Pont
		Halosulfuron methyl	Nissan/ Monsanto
		Prosulfuron	Ciba Geigy
		Primisulfuron methyl	Ciba Geigy
		Triasulfuron	Ciba Geigy

X	Y	NAME	
		Ethoxysulfuron	Agrevo
		Cyclosulfamuron	Am Cy
		Amidosulfuron	Agrevo
		DPXL 5300	Du Pont
		Nicosulfuron	Du Pont
		Rimsulfuron	Du Pont

X	Y	NAME	
		Londax	Du Pont
		Triflusulfuronmethyl	Du Pont
		Flazasulfuron	Ishihara
		Trifensulfuron methyl	Du Pont

Sulfonylurea herbicides are effective at very low doses, i.e. at a rate of application of only grams per acre. However, it is important to avoid an overdose during use. For this reason, sulfonylureas generally are used in combination with a diluent agchemical in an amount of about 20-50% by weight of the concentrate. Such diluent agchemicals usually have broad spectrum activity at a dosage rate of lbs per acre. Another advantage of using diluent agchemicals in the concentrate is that while sulfonylureas are available commercially only as solids, the diluent agchemical can be obtained in liquid form, e.g. as an emulsifiable concentrate. Accordingly, their admixture will provide a diluted liquid premix of the active for transport and use in preparing the stabilized liquid emulsifiable concentrate of the invention.

Some examples of diluent agchemicals for use herein include:

- (1) Phenoxy compounds:
e.g. phenoxy acetates (MCPA esters), phenoxy propionates, and phenoxy butyrates (MCPB esters);
- (2) Benzoates (e.g. Dicamba);
- (3) Chloroacetamide/chloroacetanilides (e.g. Alachlor, Acetachlor, and Metolachlor);
- (4) Triazine derivatives (e.g. Metribuzin), Triazinone (e.g. Metamitron);
- (5) Carbanilates (e.g. Phenmedipham);
- (6) Thiocarbamates (e.g. Thibencarb); and
- (7) Phenylurea (e.g. Linuron and Diuron).

WHAT IS CLAIMED IS:

1. A bioenhanced, stable solid carrier system for one or more sulfonyl or sulfamoyl urea active agricultural chemicals suitable for forming an aqueous microdispersed tank mix upon dilution with water, which comprises, by weight, (a) 80-99.5% of an inert matrix composition comprising 10-50% of a C₆-C₁₈ alkyl pyrrolidone, about 5-50% of an anionic surfactant and about 10-85% of a water-soluble, high melting organic compound containing a dissociable proton which can complex with said pyrrolidone, a melting point of > 100°C. a molecular weight of \leq 500, and a water solubility of at least 10%, which is selected from the group consisting of hydroxy acids, amino acids, sugars and amides, and (b) 1-20% of said active agricultural chemical, optionally with a diluent agricultural chemical.

2. A system according to claim 1 wherein said diluent agricultural chemical is present.

3. A system according to claim 1 wherein (b) comprises about 0.5-20%.

4. A system according to claim 1 wherein (b) comprises about 1-10%.

5. A system according to claim 1 wherein the organic compound comprises about 20-75%.

6. A system according to claim 1 wherein the organic compound comprises about 25-50%.

7. A system according to claim 1 wherein the anionic surfactant comprises about 10-45%.

8. A system according to claim 1 wherein the anionic surfactant comprises about 20-35%.

9. An aqueous dispersion tank mix comprising the system of claim 1 and dilution water in an amount sufficient to reduce the concentration of the agriculturally active ingredient to between a few ppm and 1% by weight.

10. A method of making the system of claim 1 which comprises admixture (a) and (b) as separate components.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/05407

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A01N 25/02, 25/22

US CL : 504/116, 118, 211-217

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 504/116, 118, 211-217

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE, APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X _E	US 5,731,264 A (NARAYANAN et al.) 24 March 1998, col. 1, lines 25-39, col. 2, lines 1-39, and col. 8, Table 1.	1-10
Y	US 5,427,795 A (FEYEN et al.) 27 June 1995, col. 1, lines 1-68, col. 2, lines 1-44.	1-10
Y _P	US 5,698,211 A (NARAYANAN) 16 December 1997, col. 2, lines 30-55, col. 12, example 7.	1-10
A	US 5,338,762 A (NARAYANAN) 16 August 1994, whole document	1-10
A	US 5,300,529 A (NARAYANAN) 05 April 1994, whole document.	1-10
Y	US 5,230,892 A (FEYEN et al.) 27 July 1993, whole document.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

27 APRIL 1998

Date of mailing of the international search report

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